

DTIC FILE COPY

②

AD-A207 769

IRON DISILICIDE THERMOELECTRIC GENERATOR

by

Philippe M. SCHLICKLIN

John G. STOCKHOLM

April 15, 1989

United States Army
EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY
London - England

Contract Number : DAJA 45 88 M 0353
TNEE

DTIC
ELECTE
MAY 11 1989
S H D

Approved for Public Release : distribution unlimited

89 5 11 075

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N° 2 Final report			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION T N E E		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) 250, route de l'Empereur 92508 RUEIL MALMAISON - FRANCE			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION European Research Office of US Army		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) 223-231 Old Marylebone Road LONDON N W 1 - 5 T H			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO. RD 5882 PH 01	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) IRON DISILICIDE THERMOELECTRIC GENERATOR					
12. PERSONAL AUTHOR(S) P.M. SCHLICKLIN - J.G. STOCKHOLM					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 8.1.88 TO 4.15.89		14. DATE OF REPORT (Year Month, Day) 1989 4 15	
15. PAGE COUNT 44					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			THERMOELECTRICITY, Thermoelectric Generators, IRON DISILICIDE		
			(AW)		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p><u>Iron disilicide</u></p> <p>A small prototype is built enabling heat flux and electrical measurements. It allows the characterization of <u>Fest</u> couples manufactured by the University of Karlsruhe (Federal Republic of Germany).</p> <p>The results on 2 couples do not confirm published data, the manufacturing of the material appears to lead to considerable quality dispersion.</p> <p>Succint sturdiness test are reported.</p> <p>Using the characterization results, a unit is dimensionned to produce between 10 and 15 watts. <u>Keywords: Semiconductors, Thermocouples,</u></p>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL John G. STOCKHOLM			22b. TELEPHONE (Include Area Code) (33) 1.47.52.58.29.		22c. OFFICE SYMBOL

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

SUMMARY

INTRODUCTION	3
1. IRON DISILICIDE COUPLES OF THE UNIVERSITY OF KARLSRUHE	4
2. DESCRIPTION OF THE EXPERIMENTAL ARRANGMENT	8
2.1. Temperature differential unit	8
2.2. Power supply for the hot source	11
2.3. External load circuit	14
2.4. Measurements and data logging	14
3. EXPERIMENTAL CHARACTERIZATION OF THE FeSi_2 COUPLES	15
3.1. Experimental procedure	15
3.2. Experimental difficulties	16
3.3. Experimental results	18
3.4. Analysis of results	23
4. DISCUSSION OF THE RESULTS AND COMPARISON WITH THE PREDICTED DATA	32
4.1. General remarks	32
4.2. Thermal properties	33
4.3. Seebeck coefficient	34
4.4. Electrical resistance and maximum generated power	35
4.5. Figure of Merit, efficiency and comparison between the measured and expected characteristics	36
5. STURDINESS TESTS	39
6. DIMENSION OF AN IRON DISILICIDE THERMOELECTRIC GENERATOR	40
6.1. Proposed couple	40
6.2. 15 watts thermoelectric generator	42
7. CONCLUSIONS	44



Accession For	
NTIC	<input checked="" type="checkbox"/>
DTIC	<input type="checkbox"/>
Unprocessed	<input type="checkbox"/>
Justification	
By	
Date	
Approved	
Dist	
A-1	

INTRODUCTION

The first study on Iron disilicide material was done by us between October 1987 and June 1988. (Project Number R-D 5 882 PH 01. Contract Number DAJA 45-87-C-0057). It covered :

- a) A theoretical study was done on the thermoelectric material Iron Disilicide. The N type is always doped with Cobalt, the P type can either be doped with Aluminium or Manganese.
- b) A small prototype was built enabling heat flux measurements. The efficiencies were measured for the Komatsu couples which have Mn doped P type legs. The unit produced with 18 couples 0.75 watt. The efficiency of a couple alone (ratio of electrical power by thermal power through the couple) was around 1 %.

This report covers the characterization of FeSi_2 couples manufactured by the University of Karlsruhe (Federal Republic of Germany). Published data indicates that this material is 2 to 3 times more performing than the Komatsu material characterized in the previous study.

Succint sturdiness test are reported.

Using the characterization results a unit is dimensionned to produce between 10 and 15 watts.

1 - IRON DISILICIDE COUPLES OF THE UNIVERSITY OF KARLSRUHE

The Institut für angewandte Physik - Institute for Applied Physics - of the University of Karlsruhe (Fed. Rep. of Germany) studied the thermoelectric material FeSi_2 in the laboratory led by Professor Ulrich BIRKHOLZ.

Two papers presented the new material :

- . Semiconducting FeSi_2 thermocouples for power generation (Ref. A)
U. Stöhrer, R. Voggesberger, G. Wagner and U. Birkholz
1st European Conference on Thermoelectrics
Cardiff Wales UK, September 1987
- . Conversion of waste exhaust heat in automobiles using FeSi_2 thermoelements (Ref. B)
U. Birkholz, E. Gross, U. Stöhrer, K. Voss, (University of Karlsruhe)
D. Gruden, W. Wurster (Porsche AG)
7th International Conference on Thermoelectric Energy Conversion,
Arlington Texas, March 1988.

1.1. ANALYSIS OF THE PUBLICATIONS

The first one (Ref. A) is more especially devoted to the material FeSi_2 and the preparation of the thermocouples. It gives the results of the measurements made on a couple, allowing to calculate the Seebeck coefficient and the electrical resistivity. Using the values of the thermal conductivity $k = 5 \text{ W/(m.k)}$ given in the second paper (Ref. B) one can reach the Figure of Merit for the material

The second publication (Ref. B) presents the experimental arrangement suited for use in a car engine. It was tested on a test bench. The two papers were analyzed in the report of the contract number RD 58 82 PH 01 dated 1988 June 15 (Chapter 5, pages 77-84). We summarize in the following tables the material characteristics deduced from the data presented in the papers (for one couple).

ΔT	T_{hot}	T_{cold}	T_{av}	Resistivity range	Seebeck coeff. α	Thermal cond. K
K	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$\mu\Omega.\text{m.}$	$\mu\text{V/K}$	W/(mK)
0	-	-	-	90.9 - 148.0	-	5
200	287	87	187	63.0 - 73.4	414	5
400	537	137	337	58.8 - 63.0	442	5
600	812	212	512	50.3 - 52.5	447	5

ΔT	Figure of Merit range $Z \times 10^4$	Open circuit voltage V_o	Maximum power P_{max}
K	K^{-1}	mV	mV
200	1.36 - 1.17	83	70
400	1.66 - 1.55	177	325
600	1.99 - 1.90	268	900

The above values are to be compared with the ones of the Komatsu material, which was experimentally studied in the previous work..

COMPARISON BETWEEN MEASURED VALUES AND CALCULATED VALUES FROM DATA OF KOMATSU

Heater Temp. °C	Effective ΔT (°C) $T_H - T_C$	Average Temp. T_{av} (°C)	Seebeck ($\mu V/K$)		Resistance (Ω)		Conductance (W/K)		$Z \times 10^4$ (K^{-1})	
			measured	Komatsu	measured	Komatsu	measured	Komatsu	measured	Komatsu
198	121	104	441	614	1.556	1.678	0.0078	0.0164	0.16	0.14
396	285	207	448	576	1.039	0.983	0.0074	0.0141	0.26	0.24
599	455	312	464	559	0.767	0.733	0.0079	0.0126	0.36	0.34
702	533	363	465	553	0.600	0.633	0.0073	0.0120	0.49	0.40
800	613	414	466	549	0.544	0.550	0.0078	0.0114	0.51	0.48

1.2. THE TWO SAMPLES OF THE UNIVERSITY OF KARLSRUHE

The University of Karlsruhe provided us with two thermoelectric couples having the same geometry as the couples described in the above mentioned papers.

The couples are marked H 208 and H 212.

The drawing of the following page gives the nominal dimensions of the couples.

The Pb-Ag solder is probably the eutectic

97.5 Pb - 2.5 Ag Melting point : 303°C

or the alloy 95 Pb - 5 Ag Liquidus 364°C Solidus 305°C

We measured the dimensions of the two samples and their electrical resistances at room temperature.

Sample	Average diameter	Cross-section for each leg	Height	Electrical resistance	Calculated resistivity
	mm	mm ²	mm	mΩ	μΩ.m.
H 208	16.20	102.25	14.9	74.42	166.3
H 212	16.25	102.88	14.8	49.97	122.5

We have an estimation of the thermal conductivity of this material by the direct measurement (using the comparative method with a standard) made on a sample provided by the University of Karlsruhe, not suitable for electricity generation.

This sample polluted by graphite during the synthesis process presented a thermal conductivity of

$$\kappa = 6.5 \text{ W/(m.k.)}.$$

Samples ⁷ H 208
H 212

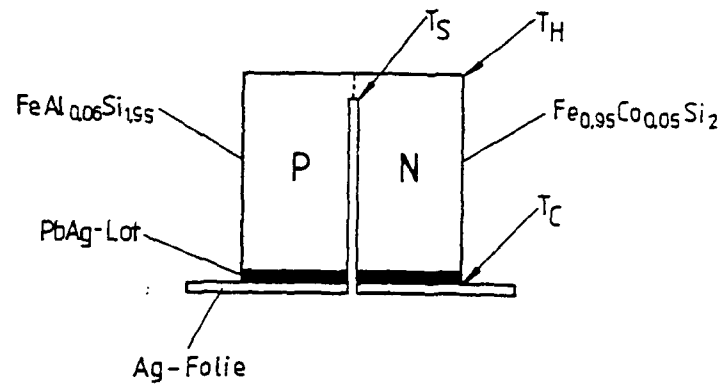


Abb. 20

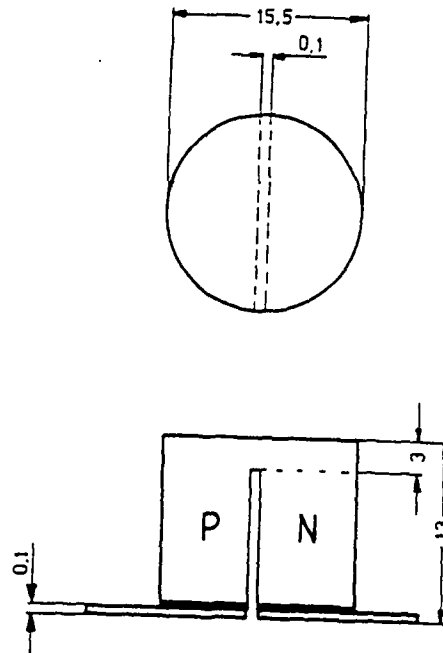


Abb. 21

2 - DESCRIPTION OF EXPERIMENTAL ARRANGEMENT

As in the report dated 1988 June 15 the experimental arrangement, built to characterize the Karlsruhe material, is very similar for its conception to the one used in the previous work done on the Komatsu material.

The arrangement composed of

- a hot source and a heat sink that constitute a temperature differential unit
- a power supply for the hot source
- an external load circuit
- an adapted instrumentation for measuring the required values and to collect the data.

2.1. TEMPERATURE DIFFERENTIAL UNIT

This unit constitutes the heart of the arrangement and comprises the hot source and the heat sink in contact with the hot and the cold junctions of the thermoelectric couples.

The geometry of the Karlsruhe couple being quite different of the one of the Komatsu couple, the temperature differential unit must be adapted to the new shape of the thermoelements and to the number of available couples, only two (2) from the University of Karlsruhe.

The photographs Fig. 2.1. and 2.2. show this unit and the drawing Fig. 2.3. gives a side half cutted view.

2.1.1. HOT SOURCE

The hot source is constituted by a parallelepipedic block of heat resistant steel (30 % Cr) Fig. 2.4. It has two parallel square faces 120 x 120 mm and a thickness of 30 mm.

Two parallel holes of 9.5 mm in diameter spaced of 40 mm are bored in the medial plane parallel to the square faces. Two high temperature heaters in a casing made of Inconel are placed into theses holes (Reference VULCANIC type 1008, 9.5 mm in diameter and 100 mm length, maximum power 500 W).

At the center of the two square faces an end facing of 2 mm in depth allows to interpose a thin mica sheet between the steel block and the thermoelectric couple, to avoid any electrical contact.

This end facing is circular of 19 mm in diameter with a small protruding area which allows the measurement of the surface temperature of the mica sheet near of the hot side of the thermoelement.

The block is put on an thick sheet of refractory and insulating material (Asbestolite) the square face being vertical and the holes for the heaters being horizontal.

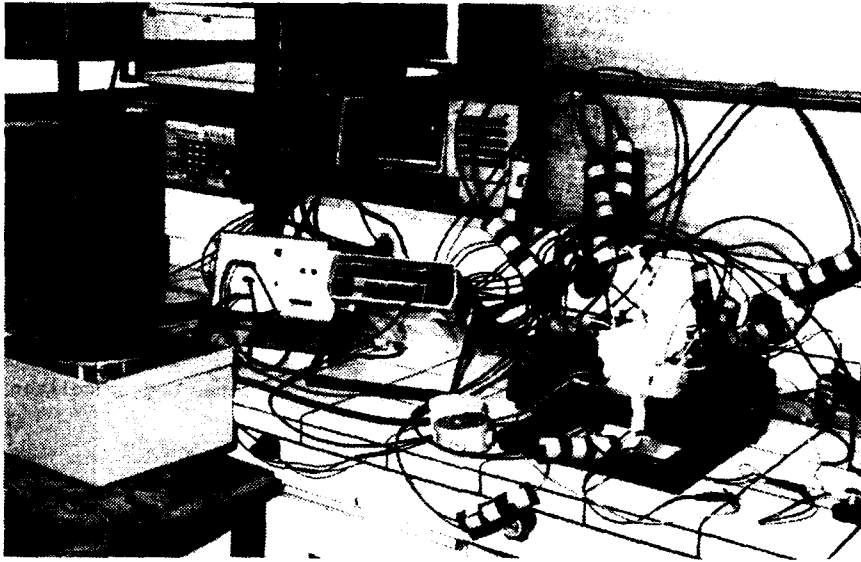


FIGURE 2.1. GENERAL VIEW OF THE EXPERIMENTAL ARRANGEMENT

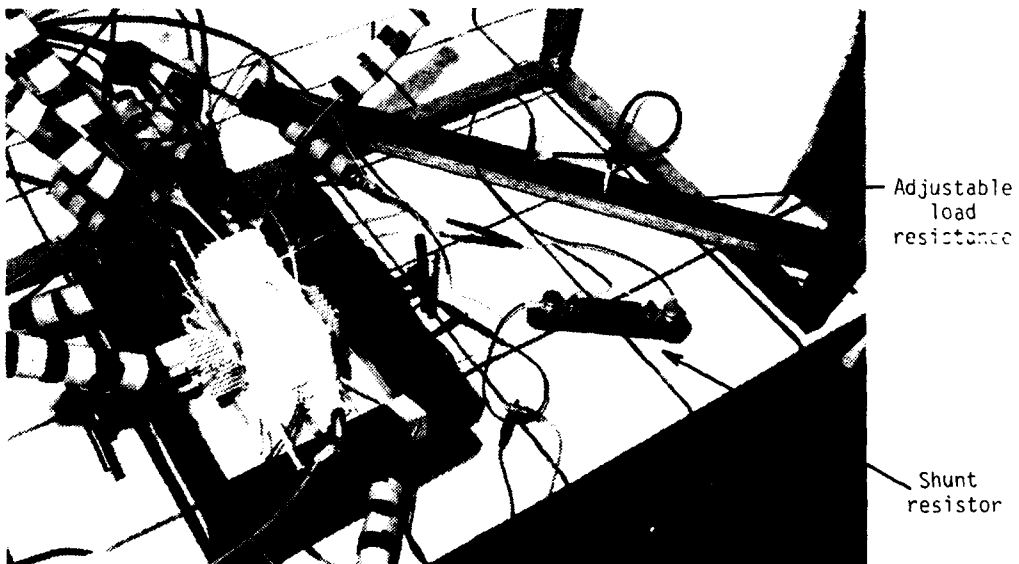
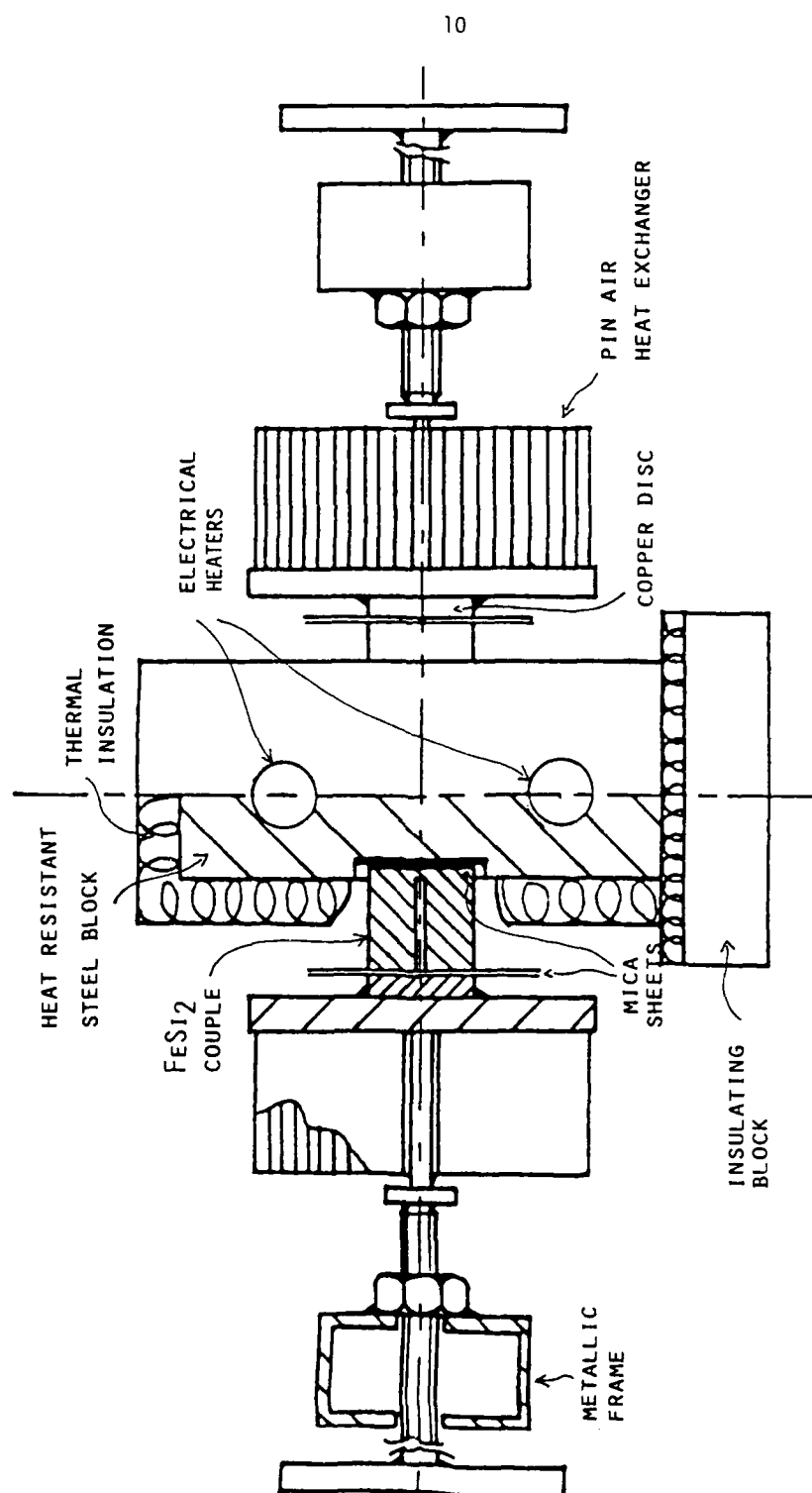


FIGURE 2.2. TEMPERATURE DIFFERENTIAL UNIT

FIG. 2.3. TEMPERATURE DIFFERENTIAL UNIT



2.1.2. COLD SOURCE

For each of the 2 tested couples, the cold source consists in a air heat exchanger which acts by natural or forced convection.

The Fig. 2.3. gives the relative position of the two air heat exchangers, with respect to the hot source block.

The heat exchangers are made of pure aluminium (1050) and obtained by extrusion process.

A heat exchanger comprises a 52 x 52 mm flat base 3 mm in thickness and an extended surface composed of 73 extruded pins 2.8 mm in diameter and 28 mm height (7 rows of 11 pins minus the 4 corner pins).

At the center of the base, a copper disc (diameter 18 mm, thickness 4 mm) is brazed using the Indalloy solder 164 (92.5 Pb, 5 In, 2.5 Ag MP = 307°C)

This disc allows to measure the temperature in a location very near the cold side of the thermoelectric couple using a thermocouple placed in a hole bored in the disc. The disc is electrically insulated from the cold side of thermoelement with a thin sheet of mica.

2.1.3. THERMAL INSULATION AND ELECTRICAL INSULATION

The whole external surface of the hot source block is insulated by a layer of ceramic fibers (Kerlane) glued by a refractory cement (Fix wool), with the exception of the small end facing surfaces and the holes for the heaters.

The thickness of the insulation is 12 to 15 mm.

For the measurements without any thermoelements two small cylinders of ceramic fibers are put into the holes provided for the thermoelements.

As mentioned above the hot and the cold side of the thermoelements are electrically insulated from the hot source and the heat sink respectively by a thin (thickness 0.10 to 0.20 mm) sheet of mica.

2.2. POWER SUPPLY FOR THE HOT SOURCE

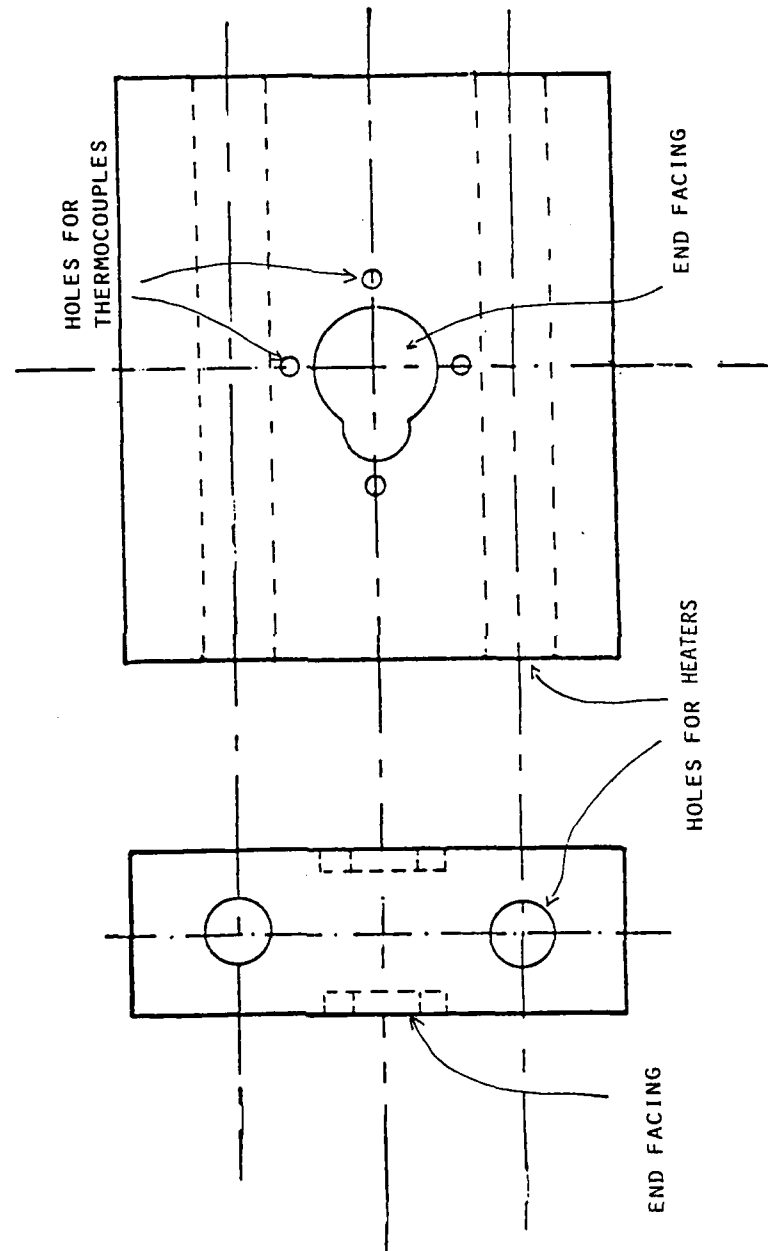
The two high temperature electrical heaters (VULCANIC 1008) are supplied in parallel by the grid (220 V AC, grounded) through an adjustable auto-transformer, which permits to obtain the appropriate value of the electrical power by variation of the input voltage between 0 and 220 V.

The input voltage is measured by a voltmeter (KEITHLEY 177).

The effective power supplied to the heaters is measured using a wattmeter giving directly the active power.

The Fig. 2.5. is a schematic of the electrical circuit including the external load circuit (see. 2.3.).

FIG. 2.4. HOT SOURCE



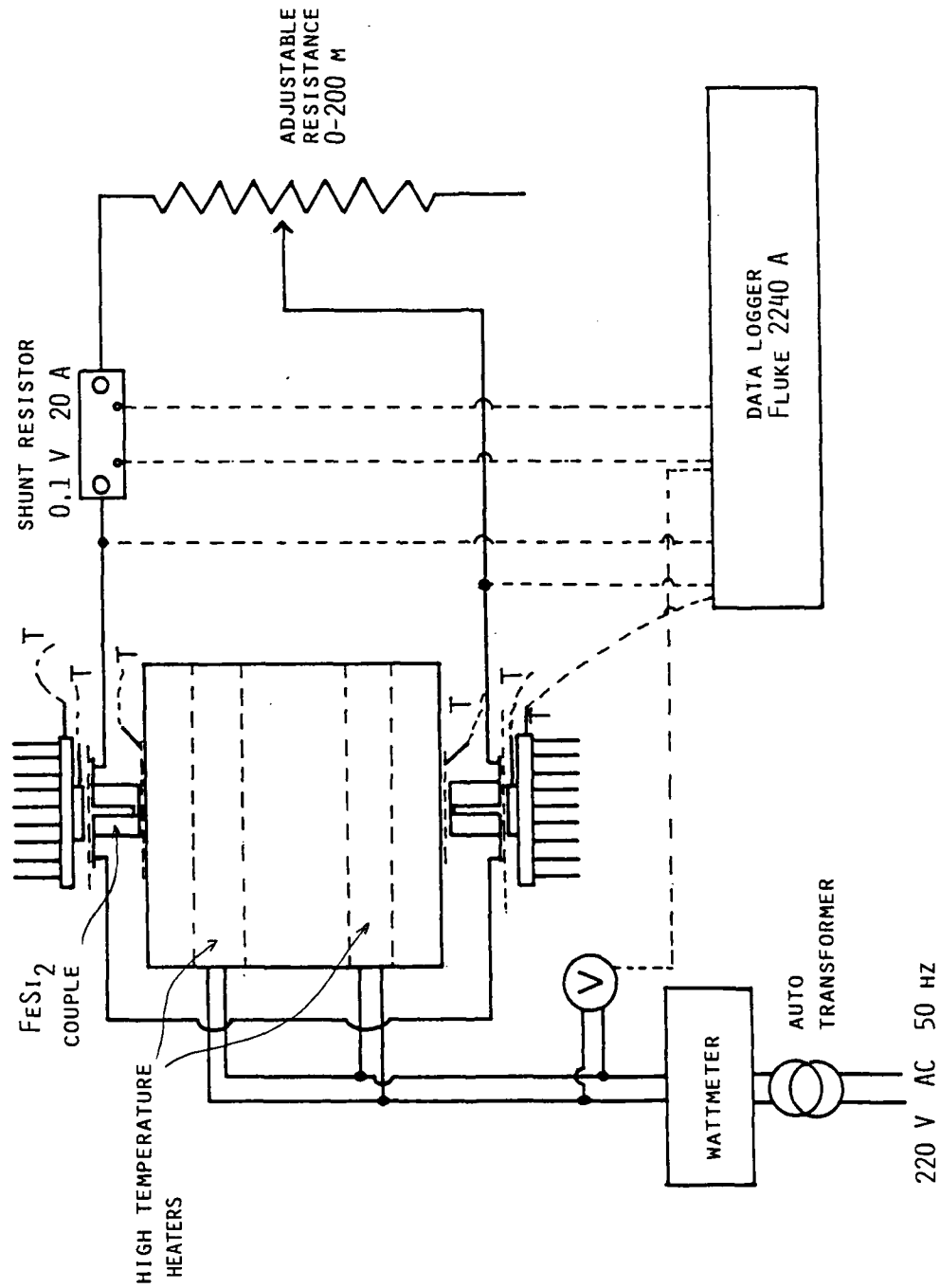


FIG. 2.5. SCHEMATIC OF THE ELECTRICAL CIRCUITS

2.3. EXTERNAL LOAD CIRCUIT

The value of the resistance of the external load circuit can be adjusted to match the internal resistance of the thermoelements, so the maximum output of the generated power can be reached.

The Karlsruhe thermoelements have a very low electrical resistance (50 and 75 mΩ at room temperature respectively) and the resistance of the wires and of the shunt resistor must be taken into account.

The adjustable part of the external load is constituted by a straight wire of a nickel-chromium alloy with a sliding contact. The total length of this wire has a resistance of 200 mΩ.

The shunt resistor (0.1 V - 20 A) with its linking wires has a resistance of 22.05 mΩ.

With the wires between the electrodes (Silver foils) brazed at the cold sides of the thermoelements, the fixed part of the external load was measured to 58.3 mΩ.

2.4. MEASUREMENTS AND DATA LOGGING

The temperature measurements are made using type K thermocouples (Chromel-Alumel) with a metallic sleeving of OPD 1.5 mm. The range of measurement is -100 + 1300°C.

- 2 sets of 4 thermocouples are inserted into holes of 5 mm deep, drilled in the hot source block in the vicinity of the end facing surfaces
- 2 sets of 3 thermocouples measure the temperature of the heat sinks : one in the copper disc and 2 in the heat exchanger for each heat sink
- 1 movable thermocouple is placed at the surface of the thermal insulation with a slight pressure.
- 2 movable thermocouples measure the mica surface temperature into the end facings.

The electrical parameters are measured as following :

- Electrical power for the hot source.
The effective power measuring device (wattmeter) gives output voltage of 0 - 10 V corresponding to the range 0-1000 W.
- External load circuit
 - . the voltage is measured directly by the data logger
 - . the current intensity is measured using a shunt resistor 0.1 V 20 A
 - . the load resistance is measured independently using an ohmmeter ESI 1701 B.

The temperatures and the electrical parameters, except the measurement of the load resistance, are linked to a data logger FLUKE, which centralizes all the data.

3 - EXPERIMENTAL CHARACTERIZATION OF THE FeSi_2 COUPLES

3.1. EXPERIMENTAL PROCEDURE

The experimental procedure is very comparable to the procedure used for the characterization of the Komatsu couples presented in the periodic report dated 1988 June 15.

The thermal properties of the couples can be approached by two sets of experiments.

A first set of experiments is made on the heater or hot source described in Chapter 2 without any thermoelements the places, of which being insulated by a small cylinder of ceramic fibers.

At steady state conditions the electrical power supplied to the resistors to maintain a given temperature of the heater is measured. These values represent the thermal losses of the assembly at various temperatures.

A second set of experiments is made with the couples in contact with the heater and the heat sink. The electrical power of the resistors is measured giving the sum of the thermal losses and the power flowing through the thermocouples, assuming that the heat losses for the same temperature of the heater are the same with and without the thermoelements.

Simultaneously the electrical parameters are measured.

First the open circuit voltage is measured for each thermoelement and for the two thermoelements in series.

Then the circuit is closed on the external load resistance. The voltage and the current intensity are measured and the generated power calculated. The external load is adjusted using the variable resistance to find the maximum generated power, which leads to the internal resistance of the thermoelectric generator.

3.2. EXPERIMENTAL DIFFICULTIES

As with Komatsu characterization, the measurement of the heat flux flowing through the thermoelements requires many precautions.

The geometry of the hot source built for the Karlsruhe couples gives greater heat losses than the previous one for Komatsu couples.

The same difficulties are encountered for the measurement of the mica surface temperature next to the hot junction of the thermoelements.

The mica surface temperature is always overestimated thus the effective ΔT is lower than the measured one.

The number of the Karlsruhe couple being limited to two and their geometry leading to a low electrical resistance - in the range of tens of $m\Omega$ - the measurement of the electrical parameters requires a very skillful assembly of the external load resistance. The fixed part of this load which comprises the wires and the shunt resistor cannot be neglected, their resistance being also in the range of tens of $m\Omega$.

At relatively high temperature (hot source over 450°C) the fixed part of the load was equal to the internal resistance of the 2 thermoelements, so the adjustable resistance was ineffective.

The fixed part of load was modified, using less resistive wire and an another shunt resistor 0.1 V 20 A ($r = 5 m\Omega$) replacing a model 0.1 V - 3A ($r = 33 m\Omega$).

The first experiments were conducted with the air heat exchangers acting in natural convection.

The poor exchange coefficient in this condition with the proximity of the hot source block leads to a limitation of the hot source temperature to around 450°C .

The limitation is the one imposed by the melting point of the solder used for connecting the cold side of thermoelements to the silver foils and the wires of the external load circuit (around 300°C).

Moreover the exchange conditions were not well defined and the dispersion in the results too great.

The experiments were then conducted using a small fan blowing on the whole temperature differential unit (air velocity near of 1.5 m/s at the air heat exchanger level). The increase of the heat exchange coefficient keeps the cold side at a reasonable temperature, below to the melting point of the solder (around 300°C) and gives the possibility of reaching a high temperature level of 800°C at the hot source

The air flow is blown also on the insulated hot source, thus the heat losses are increased. A new set of experiments was necessary to determine the heat losses of the hot source without any thermoelements in the same conditions with the air flowing on the hot source.

Another difficulty lies in the fact that the two available couples are not similar. As mentioned in Chapter 1 their electrical resistance at room temperature are 49.97 and 74.42 $m\Omega$ respectively for couples with nearly the same dimensions.

Such a difference for electrical resistance indicates that the material's other properties could present marked difference.

The experiment were thus conducted in a manner that authorize as well as possible to differentiate the two couples :

- . the temperature measurements are made at the two sides of the hot source corresponding to the two thermoelements
- . the open circuit voltage is measured for each thermoelement and for the two thermoelements in series
- . for the generated power, measured in the external load resistance, the experimental set-up allows only the measurement with the two couples in series, because the fixed part of the load has a resistance greater than the resistance of a single thermoelement.

Nevertheless, the thermal power drained by the two thermoelement being in the range of tens of watts, the accuracy of the thermal measurements, made by difference, cannot be better than $\pm 10 \%$.

For the electrical measurements, the accuracy is slightly better, but the calculations for determining the internal resistance show that the maximum of the generated power is quite difficult to find (flat extremum).

The calculation of the Seebeck coefficient, using a temperature difference, is affected by the inaccuracy of the thermal measurements.

3.3. EXPERIMENTAL RESULTS

The two sets of experiments made with the heat sink acting in natural convection are not presented here, the dispersion of the results giving an great inaccuracy in their interpretation.

The experimental values are summarized in the following tables for the experiments made in forced convection.

The temperatures are presented as following with the subscripts :
 L for left hand side corresponding to H 212 thermoelement
 R for right hand side corresponding to H 208 thermoelement
 plus the average temperature. T_{av} .

For the open circuit voltages, L and R like above plus the total value for the 2 thermoelements in series.

The table 3.1. gives the electrical power supplied to the electrical heaters needed to maintain a given temperature of the hot source without any thermoelement, but with the fan blowing on the whole assembly.

The table 3.2. gives the similar values of electrical power with the two thermoelements in contact with the hot source and the heat sinks, and the temperatures of the hot and cold sides of the thermoelements.

The electrical measurements are presented on the table 3.3. with the open voltages given by each thermoelement and the two thermoelements in series and the generated power of the two thermoelements in series.

The curves Fig. 3.1. are drawn using the values from tables 3.1. and 3.2.

For a given hot source temperature, the difference between the curve with the thermoelements and the curve without the thermoelements is the thermal power flowing through the thermoelements.

TABLE 3.1. - THERMAL MEASUREMENTS
WITHOUT THERMOELEMENTS

HEATER TEMPERATURE	MICA SURFACE TEMPERATURE °C			HEATER ELECTRICAL POWER
°C	L	R	av	PE ₀ W
198.6	145.0	140.2	142.6	37.6
349.9	270.8	240.6	255.7	81.2
496.0	381.8	356.9	369.4	136.0
595.9	481.4	476.7	479.1	181.5
696.1	582.5	545.9	564.2	241
796.8	676.6	648.7	662.7	308

Forced convection on the assembly

TABLE 3.2 - THERMAL MEASUREMENTS WITH THERMOELEMENTS

Heater Temperature °C	Mica surface temperature °C			Heat sink temperature °C			Effective delta T °C			Heater electrical power
	L	R	av.	L	R	av.	L	R	av.	PE W
98.0	71.8	68.6	70.2	28.1	29.0	28.6	43.7	39.6	41.6	31.0
197.9	150.0	145.6	147.8	36.1	34.0	35.0	113.9	111.6	112.8	48.9
347.1	283.3	270.3	276.8	50.2	53.8	52.0	233.1	216.5	224.8	101.1
449.8	341.0	361.0	351.0	62.6	68.0	65.3	278.4	293.0	285.7	145.5
496.5	358.1	354.2	356.2	67.3	74.5	70.9	290.8	279.7	285.3	164.5
596.3	435.0	460.9	447.9	83.4	90.9	87.2	351.6	370.0	360.8	220.0
696.1	562.6	580.4	571.5	96.8	108.3	102.6	465.8	472.1	468.9	283.8
792.4	678.3	652.4	665.4	109.8	120.3	115.1	568.5	532.1	550.3	348.5

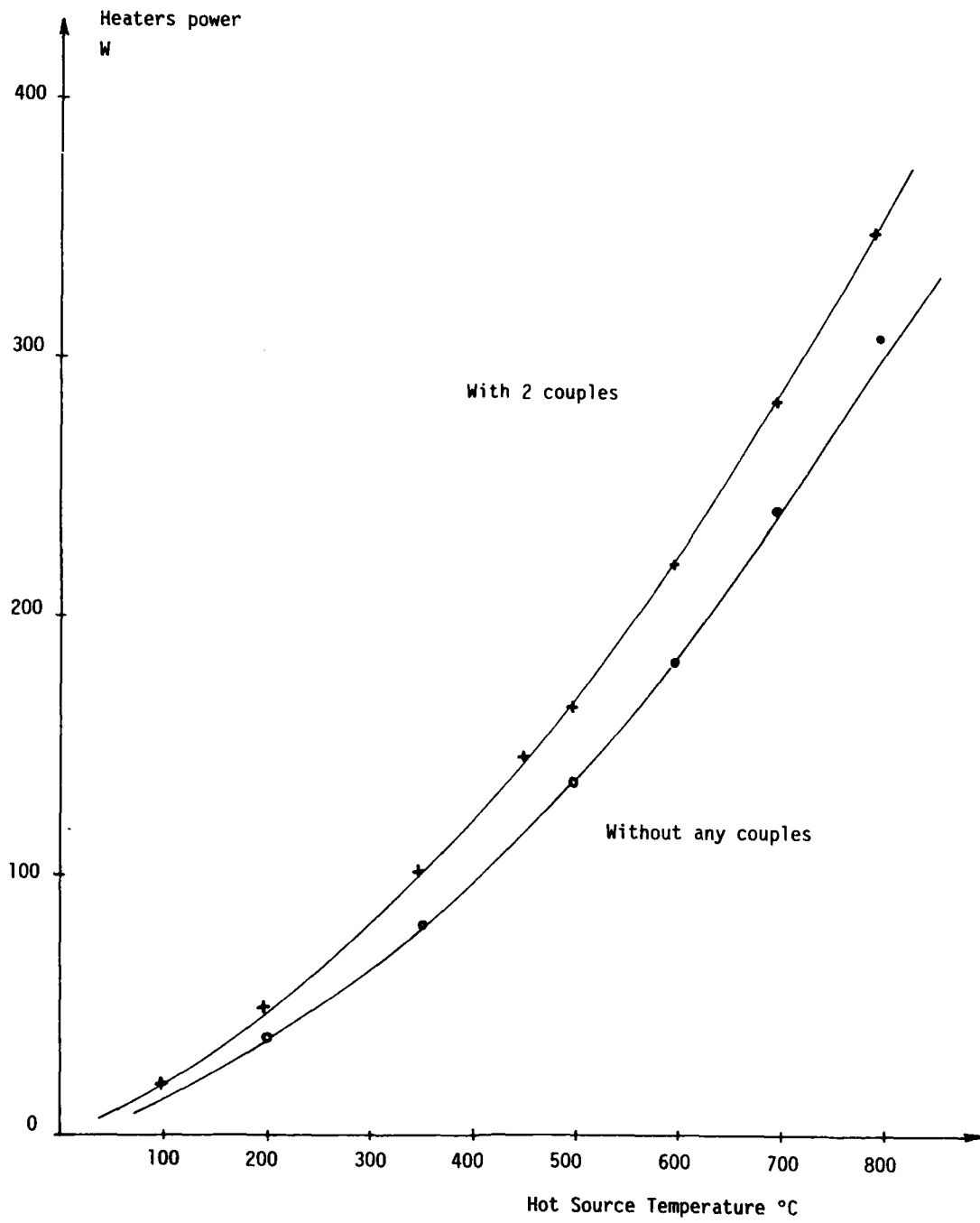
TABLE 3.3 - ELECTRICAL MEASUREMENTS

Heater Temperature °C	Effective delta T °C			Open circuit voltage mV			Maximum generated power 2 couples			
	L	R	av.	L	R	Total	R load mΩ	Voltage mV	Current A	Pmax mW
98.0	43.7	39.6	41.6	10.50	12.20	22.73	107.9 116.0 122.3	9.84 10.26 10.53	0.0915 0.096 0.0922	0.905 0.985 0.948
197.9	113.9	111.6	112.8	27.35	31.06	58.43	112.2 114.9 118.1	27.53 27.92 28.4	0.272 0.270 0.262	7.49 7.54 7.44
347.1	233.1	216.5	224.8	57.69	63.79	121.40	90.6 94.7 98.6	67.7 68.5 69.2	0.523 0.520 0.512	35.4 35.5 35.4
449.8	278.4	293.0	285.7	78.08	86.08	164.14	106.1 106.3 109.0	85.2 88.2 89.2	0.798 0.783 0.771	68.0 69.1 68.8
496.5	290.8	279.7	285.3	92.41	101.00	193.03	96.8 100.9 108.0	91.7 98.5 98.4	1.186 1.108 1.105	108.8 109.1 108.7
596.3	351.6	370.0	360.8	117.98	127.89	244.90	96.2 96.5 100.2	117.6 118.9 120.5	1.516 1.522 1.500	178.3 181.0 180.7
696.1	465.8	472.1	468.9	156.63	144.30	299.61	89.5 91.4 92.8	135.7 137.8 139.5	1.915 1.895 1.87	259.9 261.1 260.8
792.4	568.5	532.1	550.3	171.14	184.75	354.49	89.7 93.6 94.7	144.7 150.3 151.2	2.046 2.010 1.960	296.1 302.1 296.3

Forced convection on the assembly

* Maximum power

Fig. 3.1.



3.4. ANALYSIS OF RESULTS

Using the experimental values presented above, appropriate calculations lead to the characteristics of the thermoelectric couples.

3.4.1. THERMAL PROPERTIES

With the dimensions of the couples we can reach the thermal conductance and the thermal conductivity for each thermoelement.

For the thermoelement placed at left hand (H 212) :
 diameter 16-20 mm lenght 14.9 mm
 the thermal conductance can be written :

$$C_L = K_L \cdot \frac{SL}{l_L} = K_L \cdot 0.01373 \text{ (W/K)}$$

where K_L is the thermal conductivity (W/(m.K))
 and $K_L = C_L \cdot 72.86$

For the thermoelement placed right hand (H 208) :
 diameter 16.25 mm lenght 14.8 mm

$$C_R = K_R \cdot \frac{SR}{l_R} = K_R \cdot 0.01390 \text{ (W/K)}$$

or $K_L = C_L \cdot 71.94 \text{ (W/(m.K))}$.

Having no possibility of knowing the heat fluxes flowing individually through each thermoelement, we assume that the two fluxes are equal, that leads to :

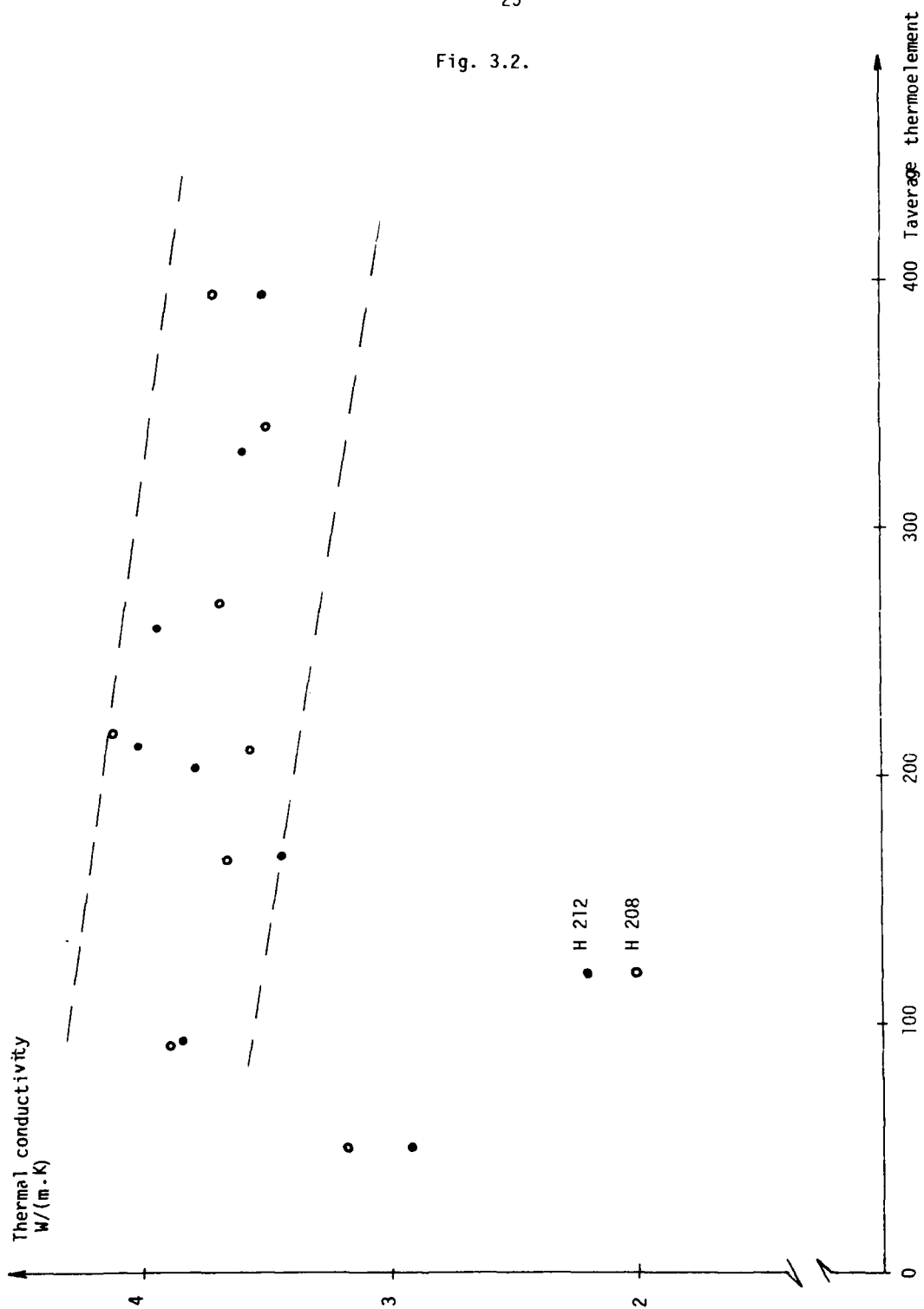
$$C_L \cdot \Delta T_L = C_R \cdot \Delta T_R = \frac{\Delta PE}{2}$$

The table 3.4. summarize the calculations and the Fig. 3.2 gives a graphical representation of the thermal conductivity for each thermoelement as a function of the average temperature of the thermoelement.

TABLE 3.4 - CALCULATION OF THE THERMAL PROPERTIES

RIGHT H 208													
LEFT H 212													
T °C HEATER	PE W	PEO W	ΔPE W	Tmca °C	Tcoold °C	ΔTL °C	CL W/K	KL W(mK)	Tmca °C	Tcoold °C	ΔTR °C	CR W/K	KR W(mK)
98.0	18.5	15.	3.5	71.8	28.1	43.7	0.04005	2.92	68.6	29.0	39.6	0.04419	3.18
197.9	47.	35.	12.	150.0	36.1	113.9	0.05268	3.84	147.8	34.0	111.6	0.05376	3.87
347.1	100.	78.	22.	283.3	50.2	233.1	0.04719	3.44	276.8	53.8	216.5	0.05081	3.66
449.8	144.	115.	29.	341.0	62.6	278.4	0.05208	3.79	351.0	68.0	293.0	0.04949	3.56
498.5	187.	135.	32.	358.1	67.3	290.8	0.05502	4.01	356.2	74.5	278.7	0.05720	4.12
596.3	220.	182.	38.	435.0	83.4	351.6	0.05404	3.94	447.9	90.9	370.0	0.05135	3.83
696.1	283.	237.	46.	562.8	96.8	465.8	0.04938	3.80	571.5	108.3	472.1	0.04872	3.50
782.4	348.	293.	55.	678.3	109.8	568.5	0.04837	3.52	685.4	120.3	532.1	0.05168	3.72

Fig. 3.2.



3.4.2. ELECTRICAL PROPERTIES

Knowing the open-circuit voltage and the corresponding difference of temperature it is easy to calculate the Seebeck coefficient.

The calculations made on the experimental values are given in the table 3.5. and the Fig. 3.3. shows the plot of the Seebeck coefficient as a function of the average temperature of the thermoelements.

The internal resistance R_i of the thermoelectric generator can be obtained by the determination of the maximum generated power P_{max} , which corresponds to the equality of the external load resistance and the internal resistance. By adjusting the load resistance as presented in the table 3.3. one can reach the values of the internal resistance.

Another calculation can be made using the relationship :

$$P_{max} = \frac{V_o^2}{4.R_i}$$

where V_o is the open circuit voltage.

Knowing a value of the internal resistance R_i and the open-circuit voltage V_o , one can calculate a value for P_{max} , which must confirm the validity of the experimental measurement.

Similarly, knowing the values of V_o and P_{max} the calculation of :

$$R_i = \frac{V_o^2}{4.P_{max}}$$

gives another values for R_i .

Theses calculations are summarized in the table 3.6.

The plot of the measured values and calculated values for the resistance R_i as function of the average temperature of the thermocouples is presented in Fig. 3.4.

The plot of the measured and calculated values of the maximum power P_{max} as a function of the difference of temperature ΔT is shown in Fig. 3.5.

TABLE 3.5 - CALCULATION OF THE SEEBECK COEFFICIENT

T Heater °C	Left H 212				Right H 208			Average couple Temperature	
	Delta TL °C	Open circuit voltage mv	Seebeck V/K	Delta TR °C	Open circuit voltage m	Seebeck V/K V	Left H212	Right H208	
98.0	43.7	10.50	240	39.6	12.20	308	50.0	48.8	
197.9	113.9	27.35	240	111.6	31.06	278	93.1	90.9	
347.1	233.1	57.69	247	216.5	63.79	295	166.8	165.3	
449.8	278.4	78.08	280	293.0	86.06	294	201.8	209.5	
496.5	290.8	92.41	318	279.7	101.0	361	212.7	215.4	
596.5	351.6	117.98	336	370.0	127.89	346	259.2	269.4	
696.1	405.8	156.63	336	472.1	144.30	306	329.7	339.9	
792.1	568.5	171.14	301	532.1	184.75	347	394.0	392.9	

Fig. 3.3.

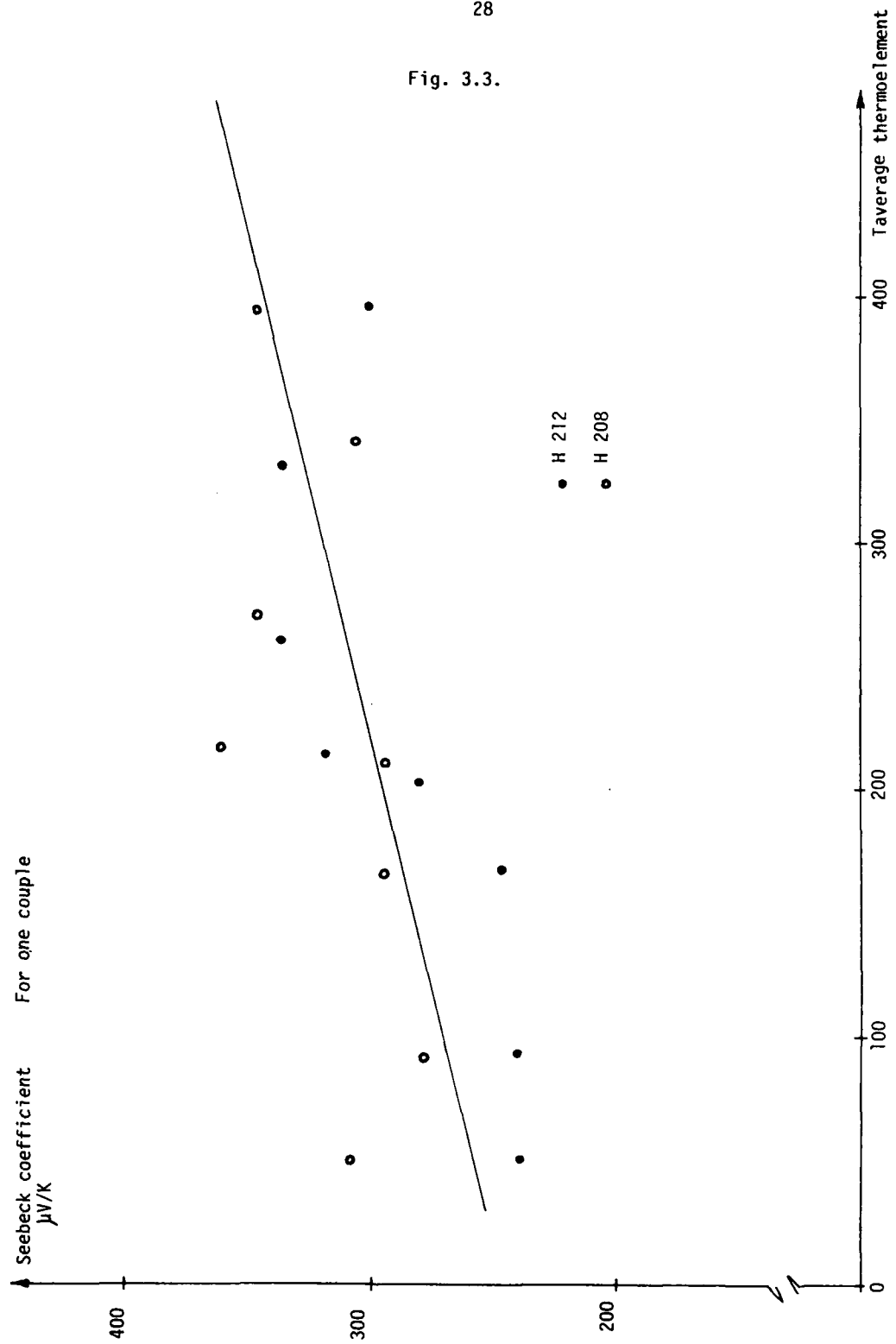


TABLE 3.6 - DETERMINATION OF THE MAXIMUM GENERATED POWER
AND THE INTERNAL RESISTANCE OF THE THERMOELEMENTS

Heater Temperature °C	R load in Ω	Maximum generated power			Open circuit voltage V_o mV	Calculated Power $P_{mar} = \frac{V_o^2}{4R}$	Calculated résistance $R = \frac{V_o^2}{4P_{max}}$	Average temperature °C	Effective Delta T °C
98.0	116.0	Voltage mV	Current A	Pmax mW	22.73	1.11	131.7	49.4	41.6
197.9	114.9	27.92	0.270	7.50	58.43	7.40	101.6	92.0	112.8
347.1	94.7	68.50	0.520	35.50	121.40	39.00	103.8	166.1	224.8
449.8	106.3	88.20	0.783	69.10	164.14	63.40	97.5	205.7	285.7
496.5	100.9	98.5	1.108	109.10	193.03	92.30	85.4	214.1	285.3
596.3	96.5	118.90	1.522	181.00	244.90	155.40	82.8	264.3	360.8
691.1	91.4	137.80	1.895	261.10	299.61	245.50	86.0	334.8	468.9
792.4	93.6	150.30	2.010	302.10	354.49	335.60	104.0	393.5	550.3

Fig. 3.4.

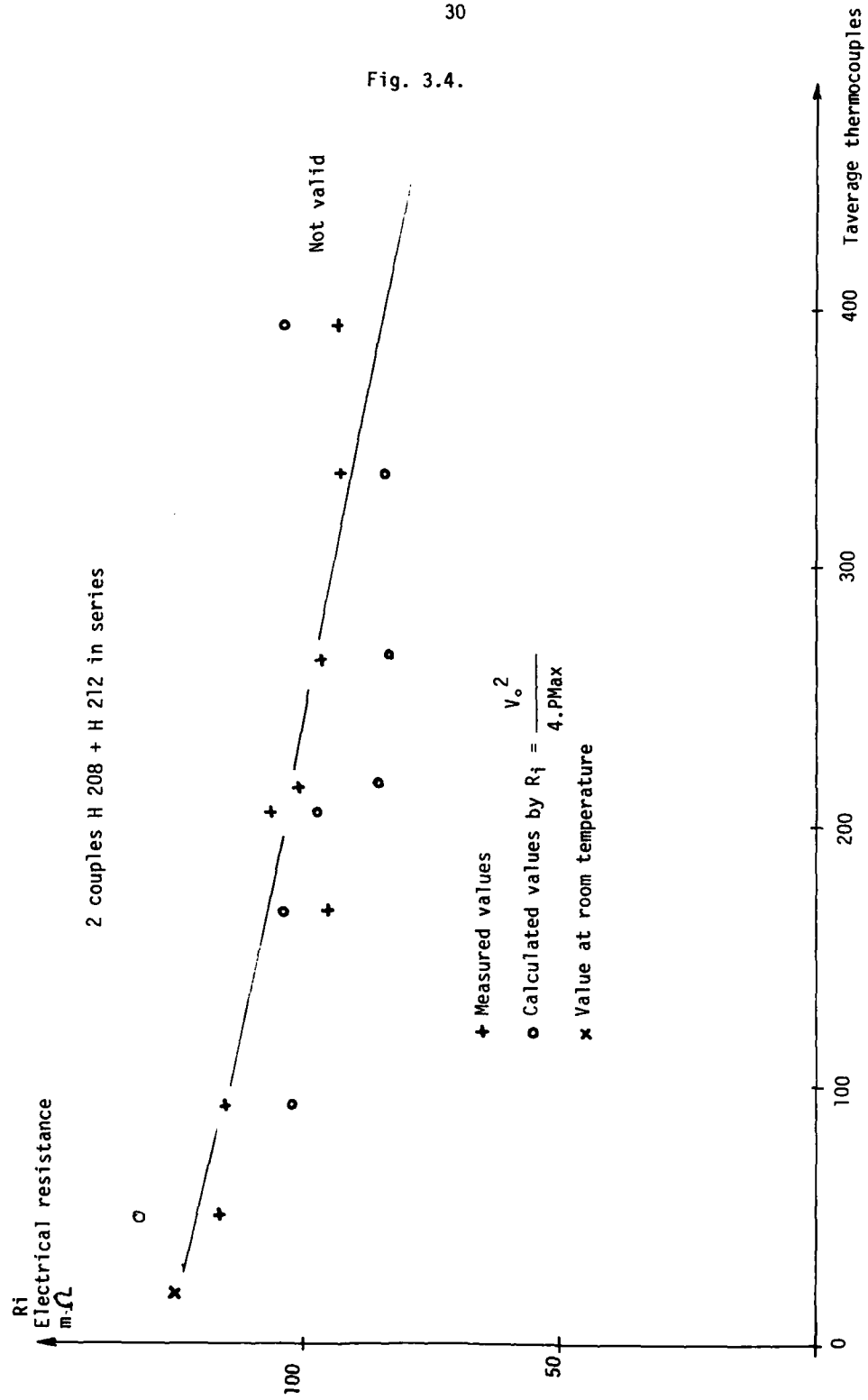
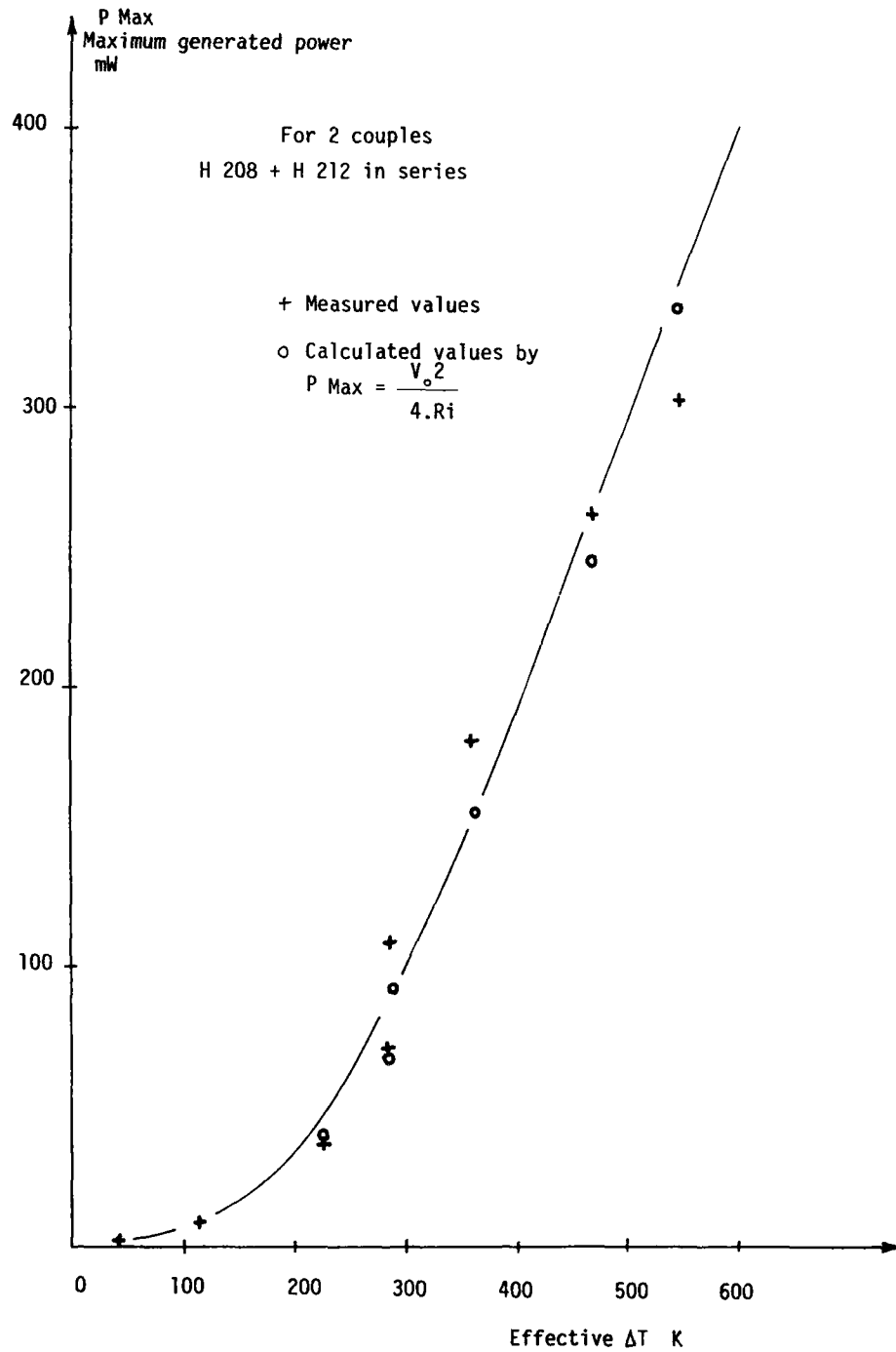


Fig. 3.5.



4 - DISCUSSION OF THE RESULTS AND COMPARISON WITH THE PREDICTED DATA

The experimental results and the successive calculations for the determination of the characteristics of the material FeSi_2 provided by the University of Karlsruhe are presented in the Chapter 3.

The present Chapter develops a discussion on these data and a comparison with the predicted data given in the two papers presented by the University of Karlsruhe.

4.1. GENERAL REMARKS

With the exception of the measured electrical powers supplied to the hot source with or without the thermoelements, which show a reasonable accuracy and give smooth curves, the graphical plots of the calculated characteristics and of the generated power present a lawness aspect.

At first sight, a trend for the variation of the characteristics as a function of the temperature seems very hard to find.

For instance, it is difficult to assert that the thermal conductivity is slightly decreasing with the temperature (Fig. 3.2.), which can explain that Professor BIRKHOLZ says that the thermal conductivity is nearly constant over the usefull range of temperature.

The experimental difficulties (see 3.2.) inherent to the measurement of very small effects explain the general dispersion, which is more sensitive at low temperature, for hot source temperature below 300°C.

Moreover the measurement with the thermoelements at a hot source temperature of 800°C are suspicious.

These measurement were fortunately conducted at the end of the set of measurements : during the disassembly of the temperature differential unit, the thermoelement H 208 was found partially debrased, so the electrical measurement made at 800°C are probably affected by this event.

Finally to determine at least the trend of the variation for the parameters, we can neglect the extreme values which are probably more suspicious i.e. the values for hot source at 100 and 800°C.

4.2. THERMAL PROPERTIES

Data from table 3.4. and Fig. 3.2..

Excluding the values for hot source at 100°C (average temperature around 50°C) which are totally out of range, the experimental points are random distributed around a straight line with a slight negative slope as a function of the average temperature T_{av} .

The dispersion is within $\pm 10\%$ and it is impossible to discriminate the two couples H 208 and H 212.

The mean values are :

- for $T_{av} = 100^\circ\text{C}$ $K = 3.95 \text{ W/(m.K)}$
- for $T_{av} = 400^\circ\text{C}$ $K = 3.8 \text{ W/(m.K)}$

The experimental value for the thermal conductivity is significantly lower than the one indicated in the papers of the University of Karlsruhe i.e. :

$$K = 5 \text{ W/(m.K)}$$

The value of the ΔT used to calculate the thermal conductivity is overestimated by the fact that the cold side temperature is measured in the copper disc brased to the air heat exchanger, the disc being electrically insulated from the thermocouple by a thin sheet of mica which induces a drop of temperature.

A correction of the experimental values has probably no sense, because the thermal resistance of the mica sheet is very bad known.

Using the data found for mica $K = 0.5 \text{ W/(m.K)}$ the value of the thermal resistance is of 1.5 K/W .

For $T_{av} = 400^\circ\text{C}$ the values of K is increased from 3.8 to 4.05 W/(m.K) . But this calculation is affected by a great inaccuracy.

4.3. SEEBECK COEFFICIENT

Data from table 3.5. and Fig. 3.3.

The value calculated for the couple H 212 at the hot source temperature of 800°C is suspicious.

The plot of the values for the Seebeck coefficient shows a slight increase as a function of the thermoelements average temperature. There are no marked difference between the two thermoelements due to the inaccuracy of the temperature measurements for the mica surface temperatures.

Like for the thermal conductivity the difference of temperature existing into the thermoelement must be greater than the one used for the calculation of the Seebeck coefficient.

As explained in the precedent paragraph a correction cannot be calculated with a reliable accuracy.

The dispersion of the value around an average value can be estimated within $\pm 15 \%$

The average values are found to be :

- at $T_{av} = 100^\circ\text{C}$ $\alpha = 275 \mu\text{V/K}$
- at $T_{av} = 400^\circ\text{C}$ $\alpha = 345 \mu\text{V/K}$

From the above mentionned publications of the University of Karlsruhe, we calculated the values of the Seebeck coefficient. The following table gives the comparison between the two sets of data.

T_{av}	U. of Karlsruhe $\alpha \mu\text{V/K}$	Present work $\alpha \mu\text{V/K} *$
187	414	295
337	442	330
512	447	371

* Using the linear relationship

$$\alpha = 252 + 0.233 \cdot t_{av}$$

t_{av} in $^\circ\text{C}$

The values calculated from experimental data are notably lower than the expected values.

The difference is approximately of 30 % at $T_{av} = 100^\circ\text{C}$ and decreases to 20 % for $T_{av} = 400^\circ\text{C}$.

4.4. ELECTRICAL RESISTANCE AND MAXIMUM GENERATED POWER

The data are taken from table 3.6. and Fig. 3.4. and 3.5.

As explained the value of the external load resistance matching the internal resistance is difficult to find. The determination of the maximum generated power is not easy by the fact that the extremum of the curve is extremely flat.

The measured values of the electrical resistance R_i plotted as a function of the average temperature for the thermoéléments (Fig. 3.4.) show an important dispersion around a straight line which begins with the value at room temperature $R_i = 125 \text{ m}\Omega$ and presents a negative slope.

The value for the hot source temperature of 792°C is not taken into account, because the debrazing of the silver foil for the thermoelement H 208 gives a parasitic resistance.

The curve of the maximum generated power P_{max} as a function of the effective ΔT (Fig. 3.5.) presents an unavoidable dispersion, but its curvature shows that the experimental results are regularly disposed on a parabolic curve as a function of the Δt . As with the resistance the value for hot source at 800°C ($\Delta T = 550^\circ\text{C}$) is suspicious

4.5. FIGURE OF MERIT, EFFICIENCY AND COMPARISON BETWEEN THE MEASURED AND EXPECTED CHARACTERISTICS

Using the averaged values for the 3 characteristics :

- thermal conductivity K (or thermal conductance C)
- electrical resistance R
- Seebeck coefficient α

the Figure of Merit of the thermoelement can be written :

$$Z = \frac{\alpha^2}{R.C.}$$

The Seebeck coefficient correspond to the sum of the Seebeck coefficient for each leg of the thermoelement : $\alpha = \alpha_N + \alpha_P$, that is the measured value.

The thermal conductance C and the electrical resistance R integrate the properties of N and P legs of the thermoelement.

The following tables summarize the characteristics, the Figure of Merit and the maximum generated power for various average material temperature T_{av} .

The upper table is relative to the measured values and the lower table gives the expected values from the papers of the University of Karlsruhe.

For both tables, the values of the Figure of Merit is obtained with the "apparent" values of thermal conductance and Seebeck coefficient calculated using the effective ΔT measured with the mica insulation.

We note a great difference between the measured values and the expected values, which were perhaps optimistic or measured on a very efficient thermoelement.

The measured characteristics lead to a Figure of Merit very close to the values measured for the Komatsu material, the lower value for the Seebeck coefficient of the Karlsruhe material being compensated by a lower value for the thermal conductance and the electrical resistivity.

COMPARISON BETWEEN MEASURED AND
EXPECTED DATA
For one couple $D=16\text{mm}$ $l = 15\text{ mm}$
Characteristics from measured and averaged data

MEASURED CHARACTERISTICS

Tav °C	K W/(mk)	C W/K	R m Ω	α $\mu\text{V/K}$	$Z \times 10^4$ K $^{-1}$	Pmax mW
100	3.95	0.0546	58.5	275	0.24	5
200	3.90	0.0539	53.0	295	0.30	35
300	3.85	0.0532	47.5	320	0.41	105
400	3.80	0.0525	42.5	345	0.53	170

EXPECTED CHARACTERISTICS

Tav °C	K W/(mk)	C W/K	R m Ω	α V/K	$Z \times 10^4$ K $^{-1}$	Pmax mW
100	5	0.0692	32.5	405	0.73	37
200	5	0.0692	29.8	415	0.84	94
300	5	0.0692	26.9	438	1.03	285
400	5	0.0692	24.2	444	1.18	430

The thermal efficiency is calculated in the following table. The values are to be compared with the values measured on the Komatsu material.

Effective ΔT K	Efficiency %
121	0.054
285	0.218
455	0.486
533	0.713
613	0.873

KOMATSU
VALUES

GENERATED POWER AND OVERALL EFFICIENCY

KARLSRUHE VALUES

			Generated power		Efficiency	
Heater temperature °C	Thermal power APE W	Effective delta T K	measured mW	calculated mW	measured %	calculated %
98.0	3.5	41.6	0.98	1.11	0.03	0.03
197.9	12.	112.8	7.5	7.4	0.06	0.06
347.1	22.	229.8	35.5	39.0	0.16	0.18
449.8	29.	285.7	69.1	63.4	0.24	0.22
496.5	32.	285.3	109.1	92.3	0.34	0.29
596.3	38.	360.8	181.0	155.4	0.47	0.41
696.1	46.	468.9	261.1	245.5	0.57	0.53
792.1	55.	550.3	302.1	335.6	0.55	0.61

In summary, the characteristics and the performances of the FeSi_2 material made by the University of Karlsruhe, are not the predicted ones.

The Figure of Merit calculated with the measured characteristics and the measured efficiency are very comparable to the same parameters of the Komatsu material.

5 - STURDINESS TESTS

The following succinct tests were done on the Komatsu couples and the couples from the University of Karlsruhe.

5.1. MECHANICAL TESTS

An unintentional shock test was done by dropping a Komatsu couple from a height of 80 cm on to a ceramic tiled floor. The couple broke near the hot junction.

In an electricity generating equipment the couples must be protected from a direct mechanical contact with outside objects.

The Komatsu couples have wiring junctions on the cold there are not sufficiently robust.

The package unit can be easily design to satisfy the MIL-shock specifications.

The University of Karlsruhe couples are more compact and are easier to strenghten.

5.2. THERMAL TESTS

The couples of University of Karlsruhe have cold junction solder which are too low temperature.

The test assembly did not permit as to reach excessive hot side temperatures.

5.3. OVERALL EVALUATION

The Iron Disilicide couples are very primitive, which is an asset.

The material is hard and brittle, so the mounting must be done intelligently.

6 - DIMENSIONS OF AN IRON DISILICIDE THERMOELECTRIC GENERATOR

6.1. PROPOSED COUPLE

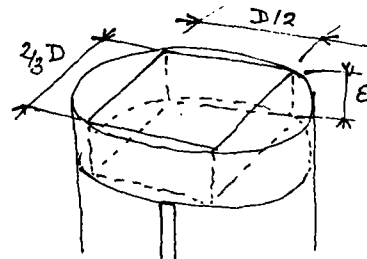
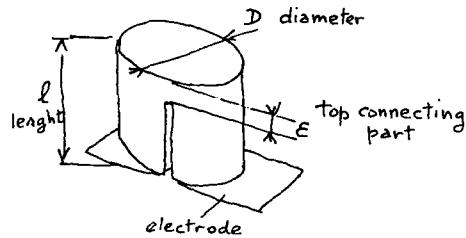
The starting point is the experimental values found on the two couples H 208 + H 212 from the University of Karlsruhe (subscript 1).

We choose a smaller couple with the same properties (subscript 2) having the same shape.

$$\text{Area } A \sim \frac{\pi D^2}{4}$$

Resistance R

Resistivity ρ



R is calculated by :

$$R = \rho \left[2 \times \frac{(1 - e)}{A/2} + \frac{D/2}{2/3 D \times E} \right]$$

2 x legs + top connecting part.

The generated power P is proportional to the ratio A/l. and to ΔT^2

We obtain for an effective $\Delta T = 550$ K at average temperature of 400°C for the material

Measured couple

$$\begin{aligned} A_1 &= 2 \text{ cm}^2 \\ D_1 &= 16 \text{ mm} \\ l_1 &= 15 \text{ mm} \\ A_1/l_1 &= 0.0133 \text{ m} \\ R_1 &= 414 \times \rho \\ R_1 &= 37.5 \text{ m}\Omega \end{aligned}$$

$$P_1 = 150 \text{ mW}$$

$$I_1 = 2 \text{ A}$$

$$V_1 = 75 \text{ mV}$$

Proposed couple

$$\begin{aligned} A_2 &= 1 \text{ cm}^2 \\ D_2 &= 11.3 \text{ mm} \\ l_2 &= 10 \text{ mm} \\ A_2/l_2 &= 0.01 \text{ m} \\ R_2 &= 810 \times \rho \\ R_2 &= 73.5 \text{ m}\Omega \end{aligned}$$

$$P_2 = P_1 \times (A_2/l_2) / (A_1/l_1)$$

$$P_2 = 112.5 \text{ mW}$$

$$I_1 = \sqrt{\frac{P_1}{R_1}} = 1.237 \text{ A}$$

$$V_2 = 90.9 \text{ mV}$$

A schematic of the proposed array is given in Fig. 5.1.

The pitches are 21.3 and 16.3 mm

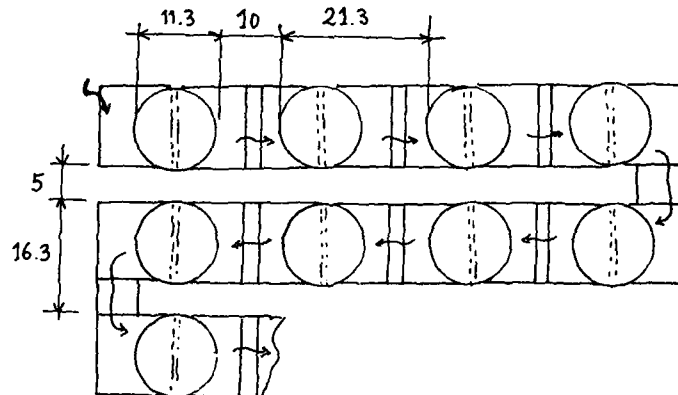


Fig. 5.1. Array for the thermoelectric couples

6.2. 15 WATTS THERMOELECTRIC GENERATOR

Using the above calculated characteristics a thermoelectric generator giving at least 15 W with a voltage of 12 V minimum can be designed.

It consists of 4 boxes which can be assembled to form a sort of chimney, as shown in Fig. 5.2.

Each box contain an array of 4 x 10 couples electrically in series, the 4 boxes being also in series.

For the effective $\Delta T = 550$ K the predicted generated power is =

$$P = 18 \text{ W and } V = 14.5 \text{ V.}$$

If the effective $\Delta T' = 450$ K the values are :

$$P' = 12 \text{ W and } V = 11.9 \text{ V}$$

$$\text{Using : } \frac{P'}{P} = \left(\frac{\Delta T'}{\Delta T} \right)^2$$

A first estimation of the mass leads to approximately 1.8 kg for a box or 7.2 kg for the unit.

15 W. IRON DISILICIDE THERMOELECTRIC GENERATOR

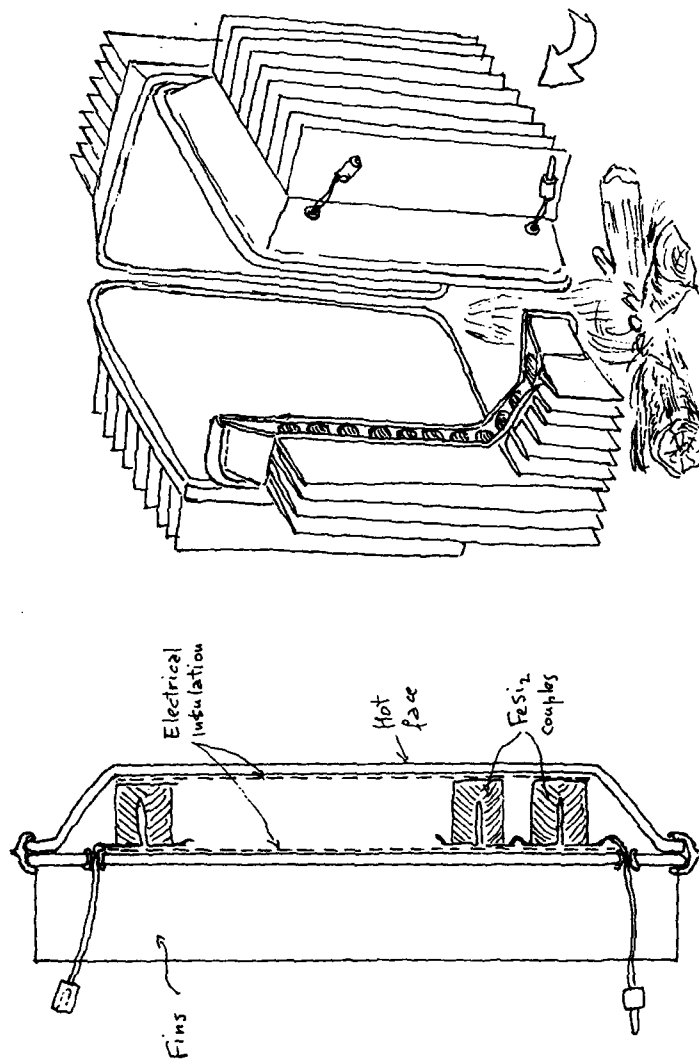


Fig. 5.2.

PS
1095

CRPAM - March 89

7 - CONCLUSIONS

The experimental characterization work was done with two couples because only two were available.

The corresponding heat fluxes were about half those required to characterize the Komatsu couples.

On top of this fact, for the Komatsu material we were dealing with 18 couples which have an averaging effect on the properties. The two couples from Karlsruhe are quite different. This was observed by their electrical resistance at room temperature.

All these made the experimentation more delicate. Several modifications had to be made on the assembly and the experiments had to be repeated before coherent results to obtain.

The conclusion is that the two couples which we have characterized have properties very similar to those of Komatsu.

These couples are from a series made by Karlsruhe for a project made in 1987. We believe the data published by Karlsruhe.

It seems there is a tremendous dispersion in the material quality of these couples. Professor Stanislas SCHERRER of the Nancy School of Mines, has underlined the fact that these couples with aluminium doping are more difficult to manufacture than the Komatsu couples with Manganese doping. The doping must be controlled with great care and requires development.

A unit to produce 15 watts using the characterized material consists of 4 parts or boxes each with an array of 4×10 couples or 160 couples. Each box would have overall dimension about $90 \times 175 \times 55$ mm and weigh approximately 1.8 kg. The overall mass for the whole unit with 4 parts would be around 7.2. kg.

Such a configuration of 4 arrays constitutes a sort of chimney.

To conclude we believe that the Karlsruhe material can have performances 2 to 3 times better than the measured one, therefore the dimensions given above could be considerably reduced.

To obtain such results a material development program over a period of about 2 years would be required;

Professor Stanislas SCHERRER of the Nancy School of Mines, who did the bibliographic study which was in the previous report of contract DAJA 45 87-C-0057 (June 88), is willing to undertake such a study.